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**(54) Method of compounding a multimodal polyethylene composition**

Verfahren zum Compoundieren einer multimodalen Polyethylenzusammensetzung

Procédé de compoundage d'une composition de polyéthylène multimodal

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**EP-A- 0 645 232** **EP-A- 0 713 889**  
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## Description

[0001] The present invention relates to a method of compounding of multimodal polyethylene compositions and more particularly to a method of compounding a multimodal polyethylene composition comprising a low molecular weight ethylene polymer and a high molecular weight ethylene polymer.

[0002] Multimodal polyethylene compositions are well known in the art. The term "multimodal" polyethylene compositions refers to the form of the molecular weight distribution curve of the composition, i.e. the appearance of the graph of the polymer weight fraction as function of its molecular weight. When a polymer is produced in a sequential step process, utilising reactors coupled in series and using different conditions in each reactor, the different fractions produced in the different reactors will each have their own molecular weight distribution. When the molecular weight distribution curves from these fractions are superimposed into the molecular weight distribution curve for the total resulting polymer product, that curve will show two or more maxima or at least be distinctly broadened in comparison with the curves for the individual fractions. Such a polymer product, produced in two or more serial steps, is called bimodal or multimodal depending on the number of steps. However, the multimodal polyethylene compositions may alternatively be produced by physical mixing of the different components prepared separately.

[0003] It is well known in the art that when producing a polymer compound that can be used for the manufacture of different objects, the ingredients thereof, such as the different polymers, additives, etc, should be mixed intimately in order to obtain a compound as homogeneous as possible. Usually, this mixing is done in a compounding device wherein the ingredients are mixed together and the polymers and optionally some of the additives are melted so that intimately mixing can occur. The melt is then extruded into a rod, cooled and granulated. In this form the resulting compound can then be used for the manufacturing of different objects.

[0004] Although the conventional compounding tools such as tandem mixer-single screw extruders and twin screw extruders, offering residence time in the order of, or shorter than, 1 minute, generally lead to acceptable quality results in compounding polymer compositions, problems are encountered when compounding multimodal polymer compositions, and more particularly multimodal polymer compositions comprising a low molecular weight ethylene polymer and a high molecular weight ethylene polymer. When compounding multimodal polymer compositions, e.g. for the manufacture of pipes, so called « white spots » occur in the compounded material. These white spots have a size of about 10-80  $\mu\text{m}$  and consist mainly of high molecular weight polymer particles that have not been adequately compounded in the composition. In addition to being disfiguring the white spots may adversely influence the strength of the composition. Further, when compounding multimodal polymer compositions, e.g. for the production of film, gel particles with a size of about 0.01-1 mm often occur. These gel particles appear as disfiguring heterogeneities in the finished film and consist mainly of high molecular weight polymer particles that have not been adequately compounded, i.e. dispersed, in the composition. The above described white spots and gel particles are a serious problem in the polymer industry and a solution to the problem would mean the removal of an obstacle to use otherwise superior multimodal polymer compositions.

[0005] WO 00/01473 A1 provides a polymer mixing device for mixing and homogenisation of polymers by elongational deformation, the device having a casing and a core defining between them a conically tapered mixing space which is divided by circumferential protrusions into slits alternating with chambers, said protrusions being arranged on the core and/or the inner wall of the casing.

[0006] US patent 6,031,027 aims to overcome this problem by providing a method of compounding a multimodal polymer composition wherein the composition is maintained at a temperature range from 10 °C below to 10 °C above the melting point of the low molecular weight polyethylene polymer during a period from 10 to 60 seconds. Such method needs a very good control of the temperature of the polymer composition and is therefore difficult to execute on the currently used industrial compounding devices.

[0007] WO 00/24821 relates to an extrusion process of particular multimodal polyethylene compositions using an extruder equipped with a gear pump. However this technology does not permit to obtain very good results with all multimodal compositions, in particular with multimodal compositions rich in low molecular weight polymer.

[0008] The present invention provides a new method of compounding multimodal polymer compositions which overcomes the above mentioned problems and which permits to obtain a very homogeneous compound which has a reduced level of white spots and/or gels and which has superior mechanical properties.

[0009] The present invention therefore relates to a method of compounding multimodal polyethylene composition in a compounding device wherein

- a) the total residence time of the polyethylene composition in the compounding device is at least 1 minute,
- b) the total drive specific energy (SEC) applied on the polyethylene composition is from 0.240 to 0.450 kWh/kg,
- c) optionally, a specific cooling energy (SCC) of at most 0.200 kWh/kg is applied on the polyethylene composition,
- d) the total specific energy, which is the difference between the total drive specific energy SEC and the specific cooling energy SCC, applied on the polyethylene composition is from 0.220 to 0.330 kWh/kg.

[0010] The present invention is related to the compounding of a multimodal polyethylene composition. For the purpose of the present invention, multimodal polyethylene composition is meant to designate compositions comprising at least a low molecular weight ethylene polymer and at least a high molecular weight ethylene polymer. For the purpose of the present invention the expression « ethylene polymer » comprises ethylene homopolymers and ethylene copolymers comprising at least 90 % by weight of units derived from ethylene. In connection with the present invention the molecular weight of the polymer is defined by way of its melt flow rate, such as measured according to ASTM 1286-90b standard. For a specific type of polymer the higher the value of its melt flow rate, the lower its mean molecular weight. Generally, the low molecular weight ethylene polymer has a melt flow rate  $MI_2$ , measured at 190 °C under a 2.16 kg load according ASTM 1286-90b, of 0.1 to 5000 g/10min, preferably from 100 to 2000 g/10min. Generally, the high molecular weight ethylene polymer has a melt flow rate HLMF, measured at 190 °C under a 21.6 kg load according ASTM 1286-90b, from 0.001 to 10.0 g/10 min, preferably from 0.001 to 1.0 g/10 min. The multimodal polyethylene compositions as determined above comprise generally from 30 to 70 % by weight of the low-molecular ethylene polymer and from 30 to 70 % by weight of the high-molecular ethylene polymer.

[0011] In the method according to the invention, the total residence time of the multimodal polyethylene composition in the compounding device is preferably at least 3 minutes, most preferably at least 4.5 minutes. Generally, the total residence time of the polyethylene composition in the compounding device does not exceed 15 minutes, preferably not 10 minutes. The total residence time of multimodal polyethylene in the compounding device is calculated based on free volume and fill factor of the compounding device, rate (polymer throughput) and density of the molten polyethylene composition (0.7636 g/ cm<sup>3</sup> at 190°C). The calculated residence time values are confirmed by a manual measurement using a colour tracer introduced at the entry of the compounding device and detected at the exit of the compounding device.

[0012] In the method according to the invention, the total drive specific energy (SEC) applied on the polyethylene composition is preferably at least 0.325 kWh/kg. Good results have been obtained when the total specific energy (SEC) applied on the polyethylene composition was at least 0.360 kWh/kg. The total drive specific energy (SEC) applied on the polyethylene composition preferably does not exceed 0.415 kWh/kg. Good results have been obtained when the total drive specific energy (SEC) applied on the polyethylene composition did not exceed 0.400 kWh/kg. In the method according to the invention, the total drive specific energy (SEC) applied on the polyethylene composition is the ratio of consumed power in the compounding device, expressed in kW, and the rate of polymer composition throughput in the compounding device, expressed in kg/h.

[0013] According to a preferred variant of the method according to the invention, the compounding device is equipped with a cooling device such that a specific cooling energy (SCC) can be applied on the polyethylene composition. The specific cooling energy (SCC) applied on the polyethylene composition is calculated from the temperature difference of the cooling medium at the inlet and outlet of the cooling device and the flow rate and specific heat capacity of the cooling medium.

[0014] In the method according to the invention, the specific cooling energy (SCC) applied on the polyethylene composition is generally lower than 0.145 kWh/kg, most preferably lower than 0.120 kWh/kg. Generally, the specific cooling energy (SCC) applied on the polyethylene composition is at least 0.045 kWh/kg, preferably at least 0.070 kWh/kg, most preferably at least 0,080 kWh/kg.

[0015] In the method according to the invention, the total specific energy, which is the difference between the total drive specific energy SEC and the specific cooling energy SCC applied on the polyethylene composition, is preferably at least 0.240 kWh/kg, most preferably at least 0.255 kWh/kg. The total specific energy applied on the polyethylene composition does preferably not exceed 0.320 kWh/kg.

[0016] The compounding device used in the method according the invention can be any equipment that, batchwise or continuously, permits to satisfy the conditions (in terms of residence time and specific energy applied to the multimodal polyethylene composition) of this method. According to a preferred embodiment of the method according to the invention, the compounding device comprises at least one melting zone preceding at least one homogenising zone.

[0017] By melting zone, it is meant to understand in the present invention, a zone wherein the specific energy applied on the polyethylene composition is kept as low as possible to strictly melt the polymer composition, without any or having as less as possible homogenising efficiency. This strict melting implies that the drive specific energy applied to the polyethylene composition in this melting zone ( $SEC_{\text{melting}}$ ) is controlled. Generally the drive specific energy applied to the polyethylene composition in the melting zone ( $SEC_{\text{melting}}$ ) does not exceed 0.260 kWh/kg, preferably not 0.240 kWh/kg. Generally, the drive specific energy applied to the polyethylene composition in this melting zone ( $SEC_{\text{melting}}$ ) is at least 0.190 kWh/kg, preferably at least 0.220 kWh/kg. The drive specific energy ( $SEC_{\text{melting}}$ ) is the ratio of consumed power in the melting equipment, expressed in kW, and the rate of polymer composition throughput in the melting zone, expressed in kg/h.

[0018] The residence time of the polyethylene composition in the melting zone is generally at least 10 seconds, preferably at least 15 seconds. The residence time of the polyethylene composition in the melting zone does generally not exceed 60 seconds, preferably not 45 seconds.

[0019] Generally, the melt temperature of the polyethylene composition coming out of the melting zone is from 210 to 260 °C, preferably from 220 to 250 °C. Most preferred the melt temperature of the polyethylene composition coming out of the melting zone is from 230 to 240 °C. The melt temperature is measured with a temperature probe immersed 2 centimetres deep in the polymer at the exit of the melting equipment.

[0020] The average shear rate applied in the melting zone is generally between 30 and 500 s<sup>-1</sup>.

[0021] By homogenising zone, it is meant to understand a zone wherein intensive homogenisation of the multimodal polyethylene composition occurs. The temperature of the polyethylene composition entering the homogenising zone is generally from 210 to 260 °C, preferably from 220 to 250 °C. Most preferred the temperature of the polyethylene composition entering the homogenising zone is from 230 to 240 °C.

[0022] The residence time of the polyethylene composition in the homogenising zone is generally at least 1 minute, preferably at least 1.5 minutes. Most preferably, the residence time in the homogenising zone is at least 3 minutes. The residence time of the polyethylene composition in the homogenising zone does generally not exceed 14 minutes, preferably not 9 minutes.

[0023] The drive specific energy applied to the polyethylene composition in the homogenising zone ( $SEC_{\text{homogenising}}$ ) does generally not exceed 0.200 kWh/kg, preferably not 0.175 kWh/kg. Generally, the drive specific energy applied to the polyethylene composition in this homogenising zone ( $SEC_{\text{homogenising}}$ ) is at least 0.100 kWh/kg, preferably at least 0.125 kWh/kg. The drive specific energy  $SEC_{\text{homogenising}}$  is the ratio of consumed power in the homogenising equipment, expressed in kW, and the rate of polymer composition throughput in the homogenising zone, expressed in kg/h.

[0024] Preferably, cooling is applied in this homogenising zone, generally through circulation of refrigerant in the envelope of the homogenising device, which at least partially compensate the specific drive energy consumption in this homogenising zone. This specific cooling energy ( $SCC_{\text{homogenising}}$ ) is generally at least 0.045 kWh/kg, preferably at least 0.070 kWh/kg and most preferably at least 0.080 kWh/kg. This specific cooling energy does generally not exceed 0.145 kWh/kg, preferably not 0.120 kWh/kg.

[0025] Generally, the melt temperature of the polyethylene composition coming out of this homogenising zone will remain below the degradation threshold. Preferably, the melt temperature of the polyethylene composition coming out of this homogenising zone is in range of 265 to 295°C and most preferably at about 275 to 285 °C. The melt temperature is measured with a temperature probe immersed 2 centimetres deep in the polymer at the exit of the homogenising equipment.

[0026] The average shear rate applied in the homogenising zone is preferably kept as low as possible. Generally, the average shear rate in the homogenising zone does not exceed 100 s<sup>-1</sup>, preferably not 50 s<sup>-1</sup>.

[0027] In this preferred embodiment of the method according to the invention, the compounding device is preferably a tandem assembly of a melting equipment and homogenising equipment. Both equipments can be exemplified by a continuous mixer or by an extruder, which may be of the single screw or twin screw type. Most preferred is a compounding device comprising a continuous mixer as melting device and an extruder, especially a single screw extruder, as homogenising device. When the homogenising device is a single screw extruder it may be constituted of classical conveying elements or it may comprise dispersive mixing elements developing shear and/or elongation stress. Preferably elements are used developing elongation stress with an application time of at least 0.5 seconds.

[0028] The compounding device used in the method according to the invention may comprise other elements currently used in known compounding devices, such as pelletizers, filters, gear pumps. In the method according to the invention a compounding device comprising no gear pump is preferably used.

[0029] The method according to the invention is very suitable for compounding multimodal polyethylene compositions comprising from 30 to 70 % by weight of low molecular ethylene polymer having a melt flow rate  $MI_2$ , measured at 190 °C under a 2.16 kg load according ASTM 1286-90b, of 1 to 5000 g/10min, preferably from 100 to 2000 g/10min, and from 30 to 70 % by weight of high molecular weight ethylene polymer having a melt flow rate  $HLMI$ , measured at 190 °C under a 21.6 kg load according ASTM 1286-90b, from 0.001 to 10.0 g/10 min, preferably from 0.001 to 1.0 g/10 min. Such multimodal polyethylene compositions are known in the art, they have for example being disclosed in US 6,136,924 and US 6,225,421. Usually the multimodal polyethylene compositions have a melt flow rate  $MI_5$ , measured at 190 °C under a 5 kg load according ASTM 1286-90b, from 0.01 to 10.0 g/10 min, preferably from 0.1 to 1.0 g/10 min and a density, measured according to ASTM D 792 standard, of 930 to 965 kg/m<sup>3</sup>, preferably of 935 to 960 kg/m<sup>3</sup>. In general, the density of the low molecular weight polyethylene present in the multimodal polyethylene composition is at least 960 kg/m<sup>3</sup>, preferably at least 965 kg/m<sup>3</sup>, most preferably at least 970 kg/m<sup>3</sup>. In general, the density of the high molecular weight polyethylene present in the multimodal polyethylene composition is from 910 to 940 kg/m<sup>3</sup>, preferably from 915 to 935 kg/m<sup>3</sup>.

[0030] The method according to the invention has been very suitable for compounding multimodal polyethylene compositions comprising from 51 to 65 % by weight of low molecular ethylene polymer having a melt flow rate  $MI_2$  higher than 100 g/10min and a density higher than 970 kg/m<sup>3</sup> and from 35 to 49 % by weight of high molecular weight ethylene polymer having a melt flow rate  $HLMI$  from 0.001 to 1.0 g/10 min and a density lower than 928 kg/m<sup>3</sup>. Usual compounding methods, such as single and twin screw extruders do generally not permit to obtain homogeneous com-

pounds of these mixtures.

[0031] The multimodal polyethylene composition used in the method according to the invention may comprise further ethylene polymers having a melt flow rate different from the low molecular weight and the high molecular weight ethylene polymers. Generally, the total quantity of these ethylene polymers does not exceed 20 %, preferably not 10 %, by weight of the multimodal polyethylene composition.

[0032] The multimodal polyethylene composition used in the invention is preferably produced in a sequential step process, utilising reactors coupled in series and using different conditions in each reactor, the different fractions produced in the different reactors will each have their own molecular weight. Alternatively, the multimodal polyethylene composition may be produced by physically mixing the different ethylene polymers prepared separately. The multimodal polyethylene composition may also be produced by a combination of both preparation methods.

[0033] In the compounding method according to the invention, the different ethylene polymers forming the multimodal polyethylene composition may be added to the compounding device at the same time. Alternatively, some of the ethylene polymers or fractions of the different ethylene polymers may be added to the compounding device in a differentiated stage during the compounding process.

[0034] Figures 1 to 5 schematically represent some possible ways to execute the method according to the invention. In figures 1 to 5, S1, S2 and S3 represent different ethylene polymers, one of which is a high molecular weight ethylene polymer and one of which is a low molecular weight ethylene polymer.

[0035] In figure 1, a multimodal polyethylene composition comprising 3 different ethylene polymers S1, S2 and S3 (obtained by sequential polymerisation or by physical mixing) is processed in compounding device comprising a melting zone M and a homogenising zone H.

[0036] In figure 2, the different ethylene polymers S1, S2 and S3 (separately polymerised) are molten in separate melting devices M1, M2 and M3 and mixed together before entering the homogenising zone H.

[0037] In figure 3, ethylene polymers S2 and S3 (separately polymerized) are molten in separate melting devices M2 and M3, mixed together before entering the homogenising zone and ethylene polymer S1 is molten in melting device M1 before addition to homogenising zone H in a differentiated stage.

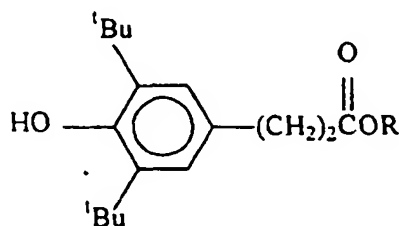
[0038] In figure 4, ethylene polymers S1 and S2 (separately polymerized) are molten in separate melting devices M1 and M2, mixed together before entering the homogenising zone and ethylene polymer S3 (in solid form) is added to homogenising zone H in a differentiated stage.

[0039] In figure 5, a mixture of ethylene polymers (obtained by sequential polymerisation or by physically mixing) is processed in the compounding device C and ethylene polymer S3 (in solid form) is processed in the compounding device C in a differentiated stage.

[0040] Additives usually added to polyethylene compositions, such as antioxidants, anti-UV agents, anti-static agents, dispersive aid agents, processing aids, pigments, ... may be added to the multimodal polyethylene composition before or during compounding. The total content of these additives does generally not exceed 10 parts, preferably not 5 parts, by weight per 100 parts by weight of multimodal polyethylene composition.

[0041] It has been surprisingly found that the addition of from 0.005 to 1 part by weight per 100 parts of multimodal polyethylene composition, of an antioxidant additive comprising a compound of formula

(I)



wherein R represents an alkyl or an alkenyl chain comprising from 8 to 35 carbon atoms, preferably from 12 to 24 carbon atoms, to the multimodal polyethylene composition permits to improve even more the homogeneity of the resulting multimodal compound so that substantially no gels appear any more. Antioxidant additives responding to formula (I) are well known. Good results have been obtained with stearyl beta-(3,5-di-t-butyl-4-hydroxyphenyl)propionate ( $R = C_{18}H_{37}$ ). Such additive is for example commercialised under the name of Irganox®1076. Especially preferred was the addition of an antioxidant additive comprising a compound of formula (I) in combination with a phosphite type antioxidant, more particularly in combination with tris(2,4-di-t-butylphenyl)-phosphite. Very good results were obtained with an antioxidant additive comprising about 20 % by weight of stearyl beta-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and about 80 % by weight of tris(2,4-di-t-butylphenyl)-phosphite. Such antioxidant additive was for example commer-

cialised under the name of Irganox®B900.

[0042] The method of compounding multimodal polyethylene compositions according to the invention offers the advantage that a homogenous compounded material, also called multimodal compound, is obtained containing a low level of white spots or gels, without substantially any degradation of the polymers present in the composition.

[0043] The quality of the multimodal compounds obtained with the compounding method described above can be measured according to ISO 13949 (1997) standard. Generally, the method according to the invention permits to obtain a dispersion quotation according to this standard which is smaller than 3, as far as the pigment and the « white spots » are concerned, and even smaller than 1.5, as far as the « white spots » are concerned. The distribution quotation usually is A2-B1, as far as the pigment and the « white spots » are concerned.

[0044] The method according to the invention permits to obtain a compound comprising a low quantity of gels. A complete gels free quality can be obtained. The presence of gels is quantified by counting the "gels" (manually or with optical cameras) on blown films having a 200 microns thickness made from the compound.

[0045] The present examples illustrate the method according to the invention.

#### Example 1 (according to the invention)

[0046] A multimodal polyethylene composition was prepared by polymerisation in two reactors disposed in series. The multimodal composition had a density of 954.0 kg/m<sup>3</sup> and a melt index MI<sub>5</sub> of 0.35 g/10min and comprised :

- 60.3 part by weight of low molecular weight polyethylene having a density of 975.1 kg/m<sup>3</sup> and a melt index MI<sub>2</sub> of 772 g/10min;
- 39.7 part by weight of high molecular weight polyethylene (ethylene-hexene copolymer) having a density of 920.2 kg/m<sup>3</sup> and a melt index HLMI of 0.1 g/10min.

[0047] To this multimodal polyethylene composition were added, for 100 parts of multimodal polyethylene composition, 0.35 part by weight of antioxidant IRGANOX® B225, 0.10 part by weight of calcium stearate and 2.25 parts by weight of carbon black.

[0048] This additivated composition was extruded on a compounding device comprising a melting zone (single screw extruder, 90mm screw diameter, 24D length) and a homogenising zone (single screw extruder, 90 mm diameter screw, 36D length) according to the conditions specified in table 1. At the end of the compounding device, the resulting compound was passed through a strand pelletizer and pellets of the resulting compound were recuperated and examined. The results obtained are presented in table 2.

#### Example 2 (according to the invention)

[0049] Example 1 was reproduced under the conditions specified in table 1, by adding to the multimodal composition of example 1, per 100 parts by weight of multimodal polyethylene composition : 0.35 part by weight of antioxidant IRGANOX® B225, 0.25 part by weight of antioxidant IRGANOX® B900, 0.10 part by weight of calcium stearate and 2.25 parts by weight of carbon black.

#### Example 3 and 4 (according to the invention)

[0050] A multimodal polyethylene composition was prepared by polymerisation in two reactions disposed in series having a density of 955.6 kg/m<sup>3</sup> and a melt index MI<sub>5</sub> of 0.6 g/10min and comprising :

- 59.5 part by weight of low molecular weight polyethylene having a density of 973.5 kg/m<sup>3</sup> and a melt index MI<sub>2</sub> of 581 g/10min;
- 40.5 part by weight of high molecular weight polyethylene (ethylene-hexene copolymer) having a density of 930.6 kg/m<sup>3</sup> and a melt index HLMI of 0.2 g/10min.

[0051] To this multimodal polyethylene composition were added, for 100 parts by weight of multimodal polyethylene composition, 0.35 part by weight of antioxidant IRGANOX® B225, 0.10 part of calcium stearate and 2.25 parts of carbon black.

[0052] This additivated composition was extruded on the compounding device described in Example 1 according to the conditions specified in table 1. The results obtained are presented in table 2.

Comparative Example 4R (not according to the invention)

[0053] The additivated multimodal composition described in example 1 was extruded on a twin screw extruder (commercial Werner® ZSK 40 extruder, run in adiabatic mode, comprising a twin screw of 40 mm diameter, 26D length) and a strand pelletizer, in the conditions specified in Table 3.

[0054] The properties of the resulting compound are presented in table 4.

Comparative Examples 5R, 6R, and 7R (not according to the invention)

[0055] The additivated composition described in example 3 was extruded on a twin screw extruder (commercial Werner® ZSK 40 extruder, run with controlled temperature profile, comprising a twin screw of 40 mm diameter, 26D length) and a strand pelletizer, in the conditions specified in table 3.

[0056] The properties of the resulting compound are presented in Table 4.

Table 1

Ex	Rate kg/h	Melting zone			Homogenising zone			Total residence time s	Total SEC kWh/ kg	Total specific energy applied (SEC-SCC)
		screw speed rpm	SECmelting kWh/kg	t° melt out °C	screw speed rpm	SEC <sub>homogenising</sub> kWh/kg	SEC <sub>homogenising</sub> kWh/kg			
1	75	112	0.231	239	30	0.139	0.090	273	0.370	0.280
2	75	112	0.234	239	30	0.156	0.105	276	0.390	0.285
3	75	112	0.224	233	30	0.140	0.080	275	0.362	0.282
4	100	150	0.250	236	40	0.140	0.073	283	0.390	0.317



Table 2

Ex.	Pigment dispersion ISO 13949	White spot dispersion ISO 13949	Pigment distribution ISO 13949	Gels on 20 micron films number/kg
1	2.3	1.0	A2	17700
2	2.5	1.0	A2	2300
3	2.5	1.0	A2	6250
4	4.2	1.5	B1	9850

Table 3

Ex.	Rate kg/h	Total residence time s	Twin screw extruder		
			screw speed rpm	SEC <sub>melting</sub> kW/h/kg	t° melt °C
4R	7	45	150	0.260	277
5R	20	20	330	0.265	263
6R	30	20	330	0.260	261
7R	40	20	330	0.255	257

Table 4

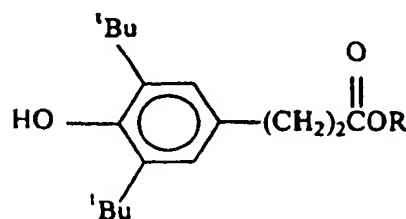
Ex.	White spot dispersion ISO 13949	Pigment distribution ISO 13949	Gels on 20 micron films number/kg
4R	10	C2	countless
5R	7	C1	12600
6R	10	D1	36100
7R	15	D2	countless

## Claims

1. Method of compounding a multimodal polyethylene composition in a compounding device comprising a tandem assembly of a melting equipment and homogenising equipment, wherein

- a) the total residence time of the polyethylene composition in the compounding device is at least 1 minute,
- b) the total drive specific energy (SEC) applied on the polyethylene composition is from 0.240 to 0.450 kWh/kg,
- c) optionally, a specific cooling energy (SCC) of at most 0.200 kWh/kg is applied on the polyethylene composition,
- d) the total specific energy, which is the difference between the total drive specific energy SEC and the specific cooling energy SCC, applied on the polyethylene composition is from 0.220 to 0.330 kWh/kg.

2. Method according to claim 1, wherein the total residence time of the polyethylene composition in the compounding device is at least 3 minutes.
3. Method according to claim 1 or 2, wherein the total drive specific energy (SEC) applied on the polyethylene composition is from 0.325 to 0.415 kWh/kg and wherein the specific cooling energy (SCC) applied on the polyethylene composition is from 0.045 to 0.145 kWh/kg.
4. Method according to any one of claims 1 to 3, wherein the compounding device comprises at least one melting zone preceding at least one homogenising zone.
5. Method according to claim 4, wherein the drive specific energy applied to the composition in the melting zone ( $SEC_{\text{melting}}$ ) is from 0.190 to 0.260 kWh/kg.
6. Method according to claim 4 or 5, wherein the temperature of the composition coming out of the melting zone and entering the homogenising zone is from 210 to 260 °C.
7. Method according to any one of claims 4 to 6, wherein the residence time of the polyethylene composition in the homogenising zone is at least 1,5 minutes.
8. Method according to any one of claims 4 to 7, wherein the drive specific energy applied to the polyethylene composition in the homogenising zone ( $SEC_{\text{homogenising}}$ ) is from 0.100 to 0.200 kWh/kg and wherein a specific cooling energy ( $SCC_{\text{homogenising}}$ ) from 0.045 to 0.145 kWh/kg is applied on the polyethylene composition in the homogenising zone.
9. Method according to any one of claims 4 to 8, wherein the temperature of the composition coming out of the homogenising zone is from 265 to 295 °C.
10. Method according to any one of claims 4 to 9, wherein the homogenising zone comprises a single screw extruder.
11. Method according to claim 10, wherein the single screw extruder comprises mixing elements developing shear and/or elongation stress.
12. Method according to anyone of claims 1 to 11, wherein from 0.005 to 1 part, per 100 parts of multimodal polyethylene composition, of a antioxidant additive comprising a compound of formula

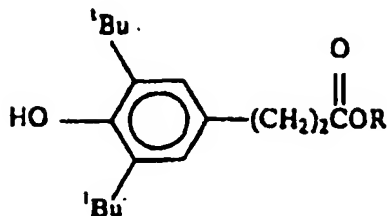


wherein R represents an alkyl or an alkenyl chain comprising from 8 to 35 carbon atoms, is added to the multimodal polyethylene composition.

13. Method according to anyone of claims 1 to 12 wherein the multimodal polyethylene composition has a melt flow rate  $MI_5$  from 0.01 to 10.0 g/10 min and a density of 930 to 965 kg/m<sup>3</sup> and comprises from 30 to 70 % by weight of a low molecular weight ethylene polymer having a melt flow rate  $MI_2$  from 1 to 5000 g/10 min and a density of at least 960 kg/m<sup>3</sup>, and from 30 to 70 % by weight of a high molecular weight ethylene polymer having a melt flow rate HLMF from 0.001 to 10.0 g/10 min and a density of 910 to 940 kg/m<sup>3</sup>.
14. Method according to any preceding claim, wherein the average shear rate applied in the homogenising zone does not exceed 100 s<sup>-1</sup>, preferably not 50 s<sup>-1</sup>.

## Patentansprüche

1. Verfahren zum Compoundieren einer multimodalen Polyethylenzusammensetzung in einer Compoundierungsvorrichtung, umfassend eine Tandemanordnung einer Schmelzausrüstung und Homogenisierungsausrüstung, worin
  - a) die Gesamtverweilzeit der Polyethylenzusammensetzung in der Compoundierungsvorrichtung mindestens 1 Minute ist,
  - b) die spezifische Gesamtantriebsenergie (SEC), die auf die Polyethylenzusammensetzung angewendet wird; 0,240 bis 0,450 kWh/kg ist,
  - c) gegebenenfalls eine spezifische Kühlenergie (SCC) von maximal 0,200 kWh/kg auf die Polyethylenzusammensetzung angewendet wird,
  - d) die spezifische Gesamtenergie, welche die Differenz zwischen der spezifischen Gesamtantriebsenergie SEC und der spezifischen Kühlenergie SCC ist, die auf die Polyethylenzusammensetzung angewendet wird, 0,220 bis 0,330 kWh/kg ist.
2. Verfahren nach Anspruch 1, wobei die Gesamtverweilzeit der Polyethylenzusammensetzung in der Compoundierungsvorrichtung mindestens 3 Minuten ist.
3. Verfahren nach Anspruch 1 oder 2, wobei die spezifische Gesamtantriebsenergie (SEC), die auf die Polyethylenzusammensetzung angewendet wird, 0,325 bis 0,415 kWh/kg ist und wobei die spezifische Kühlenergie (SCC), die auf die Polyethylenzusammensetzung angewendet wird, 0,045 bis 0,145 kWh/kg ist.
4. Verfahren nach einem der Ansprüche 1 bis 3, wobei die Compoundierungsvorrichtung mindestens eine Schmelzzone, die der mindestens einen Homogenisierungszone vorangeht, umfasst.
5. Verfahren nach Anspruch 4, wobei die spezifische Antriebsenergie, die auf die Zusammensetzung in der Schmelzzone ( $SEC_{\text{Schmelze}}$ ) angewendet wird, 0,190 bis 0,260 kWh/kg ist.
6. Verfahren nach Anspruch 4 oder 5, wobei die Temperatur der Zusammensetzung, die aus der Schmelzzone herauskommt und in die Homogenisierungszone gelangt, 210 bis 260°C ist.
7. Verfahren nach einem der Ansprüche 4 bis 6, wobei die Verweilzeit der Polyethylenzusammensetzung in der Homogenisierungszone mindestens 1,5 Minuten ist.
8. Verfahren nach einem der Ansprüche 4 bis 7, wobei die spezifische Antriebsenergie, die auf die Polyethylenzusammensetzung in der Homogenisierungszone ( $SEC_{\text{Homogenisierung}}$ ) angewendet wird, 0,100 bis 0,200 kWh/kg ist, und wobei eine spezifische Kühlenergie ( $SCC_{\text{Homogenisierung}}$ ) von 0,045 bis 0,145 kWh/kg auf die Polyethylenzusammensetzung in der Homogenisierungszone angewendet wird.
9. Verfahren nach einem der Ansprüche 4 bis 8, wobei die Temperatur der Zusammensetzung, die aus der Homogenisierungszone herauskommt, 265 bis 295°C ist.
10. Verfahren nach einem der Ansprüche 4 bis 9, wobei die Homogenisierungszone einen Einschneckenextruder umfasst.
11. Verfahren nach Anspruch 10, wobei der Einschneckenextruder Mischelemente, die Scher- und/oder Dehnungsspannung entwickeln, umfasst.
12. Verfahren nach einem der Ansprüche 1 bis 11, wobei 0,005 bis 1 Teil, pro 100 Teile der multimodalen Polyethylenzusammensetzung von einem Antioxidanzadditiv, das eine Verbindung der Formel umfasst



worin R eine Alkyl- oder eine Alkenylkette, umfassend 8 bis 35 Kohlenstoffatome, wiedergibt, zu der multimodalen Polyethylenzusammensetzung gegeben wird.

13. Verfahren nach einem der Ansprüche 1 bis 12, wobei die multimodale Polyethylenzusammensetzung eine Schmelzflussrate  $MI_5$  von 0,01 bis 10,0 g/10 min und eine Dichte von 930 bis 965 kg/m<sup>3</sup> aufweist, und 30 bis 70 Gewichtsprozent eines Ethylenpolymers mit niedrigem Molekulargewicht mit einer Schmelzflussrate  $MI_2$  von 1 bis 5000 g/10 min und einer Dichte von mindestens 960 kg/m<sup>3</sup> und 30 bis 70 Gewichtsprozent eines Ethylenpolymers mit hohem Molekulargewicht mit einer Schmelzflussrate  $HLMI$  von 0,001 bis 10,0 g/10 min und einer Dichte von 910 bis 940 kg/m<sup>3</sup> umfasst.

14. Verfahren nach einem vorangehenden Anspruch, wobei die auf die Homogenisierungszone angewendete mittlere Scherrate 100 s<sup>-1</sup>, vorzugsweise 50 s<sup>-1</sup>, nicht übersteigt.

## Revendications

1. Procédé de mélange d'une composition de polyéthylène multimodal dans un dispositif de mélange comprenant un montage en tandem associant un équipement de fusion et un équipement d'homogénéisation, dans lequel

- a) le temps de séjour total de la composition de polyéthylène dans le dispositif de mélange est d'au moins 1 minute,
- b) l'énergie spécifique d'actionnement (SEC) totale appliquée à la composition de polyéthylène est de 0,240 à 0,450 kWh/kg,
- c) de façon facultative, une énergie spécifique de refroidissement (SCC) d'au maximum 0,200 kWh/kg est appliquée à la composition de polyéthylène,
- d) l'énergie spécifique totale, qui correspond à la différence entre l'énergie spécifique d'actionnement (SEC) totale et l'énergie spécifique de refroidissement (SCC), appliquée à la composition de polyéthylène, est de 0,220 à 0,330 kWh/kg.

2. Procédé selon la revendication 1, dans lequel le temps de séjour total de la composition de polyéthylène dans le dispositif de mélange est d'au moins 3 minutes.

3. Procédé selon les revendications 1 ou 2, dans lequel l'énergie spécifique d'actionnement (SEC) totale appliquée à la composition de polyéthylène est de 0,325 à 0,415 kWh/kg et dans lequel l'énergie spécifique de refroidissement (SCC) appliquée à la composition de polyéthylène est de 0,045 à 0,145 kWh/kg.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le dispositif de mélange comprend au moins une zone de fusion précédant au moins une zone d'homogénéisation.

5. Procédé selon la revendication 4, dans lequel l'énergie spécifique d'actionnement appliquée à la composition dans la zone de fusion ( $SEC_{fusion}$ ) est de 0,190 à 0,260 kWh/kg.

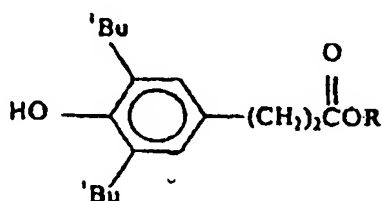
6. Procédé selon les revendications 4 ou 5, dans lequel la température de la composition à la sortie de la zone de fusion et à l'entrée dans la zone d'homogénéisation est de 210 à 260°C.

7. Procédé selon l'une quelconque des revendications 4 à 6, dans lequel le temps de séjour de la composition de polyéthylène dans la zone d'homogénéisation est d'au moins 1,5 minute.

8. Procédé selon l'une quelconque des revendications 4 à 7, dans lequel l'énergie spécifique d'actionnement appli-

quée à la composition de polyéthylène dans la zone d'homogénéisation ( $SEC_{\text{homogénéisation}}$ ) est de 0,100 à 0,200 kWh/kg et dans lequel une énergie spécifique de refroidissement ( $SCC_{\text{homogénéisation}}$ ) de 0,045 à 0,145 kWh/kg est appliquée à la composition de polyéthylène dans la zone d'homogénéisation.

- 5 9. Procédé selon l'une quelconque des revendications 4 à 8, dans lequel la température de la composition à la sortie de la zone d'homogénéisation est de 265 à 295°C.
- 10 10. Procédé selon l'une quelconque des revendications 4 à 9, dans lequel la zone d'homogénéisation comprend une extrudeuse à une vis.
11. Procédé selon la revendication 10, dans lequel l'extrudeuse à une vis comprend des éléments mélangeurs appliquant des contraintes de cisaillement et/ou d'allongement.
12. Procédé selon l'une quelconque des revendications 1 à 11, dans lequel de 0,005 à 1 partie, pour 100 parties de composition de polyéthylène multimodal, d'un additif antioxydant comprenant un composé de formule



dans laquelle R représente une chaîne alkyle ou alcényle comprenant de 8 à 35 atomes de carbone, est ajoutée à la composition de polyéthylène multimodal.

- 30 13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel la composition de polyéthylène multimodal présente un indice de fusion  $MI_5$  de 0,01 à 10,0 g/10 min et une masse volumique de 930 à 965 kg/m<sup>3</sup>, et comprend de 30 à 70 % en poids d'un polymère d'éthylène de faible poids moléculaire, présentant un indice de fusion  $MI_2$  de 1 à 5 000 g/10 min et une masse volumique d'au moins 960 kg/m<sup>3</sup>, ainsi que de 30 à 70 % en poids d'un polymère d'éthylène de poids moléculaire élevé présentant un indice de fusion HLMI de 0,001 à 10,0 g/10 min et une masse volumique de 910 à 940 kg/m<sup>3</sup>.
- 35 14. Procédé selon l'une quelconque des revendications précédentes, dans lequel le taux de cisaillement moyen appliqué dans la zone d'homogénéisation ne dépasse pas 100 s<sup>-1</sup> et, de préférence, 50 s<sup>-1</sup>.

